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CLAIMS

[Claim(s)]

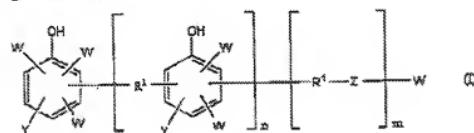
[Claim 1] Metal surface treatment containing metallic compounds (c) characterized by comprising the following.:

A resin compound expressed with general formula (I) (a).

At least one sort of vanadium compounds (b).

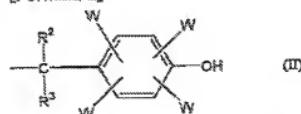
At least one sort of metal chosen from a group which consists of a zirconium, titanium, molybdenum, tungsten, manganese, and cerium.

[Formula 1]



Each R¹ expresses -CH₂-, -CH₂-NH-CH₂-, or -CH=N-CH₂- mutually-independent among {type, and Y is a hydrogen atom or general formula (II).

[Formula 2]



It means (R² and R³ express the alkyl group of a hydrogen atom or the carbon numbers

1-3 mutually-independent among a formula). Z was made by losing the hydrogen atom combined with the carbon atom which constitutes the aromatic ring from aromatic compounds which can carry out addition condensation to formaldehyde. It may have 1-4 bases- CH_2X (X in a formula is synonymous with X under definition of the below-mentioned W). Whether the aromatic ring group in the structure bundled with n is a different divalent basis, melamine, It is the divalent basis made by losing one hydrogen atom at a time from two amino groups, guanamine or urea, W is a hydrogen atom or the basis P each mutually-independent — this — P- CH_2X . — The inside of a $\text{OH}_2\text{NCH}_2\text{X}$ or $-\text{CH}=\text{NCH}_2\text{X}$ [type and X are OH, OR⁴ (R⁴ expresses the alkyl group of the carbon numbers 1-5, or the hydroxyalkyl group of the carbon numbers 1-5), a halogen atom, general formula (III), or (IV).

[Formula 3]



the inside of a formula, R^5 , R^6 , R^7 , R^8 , and R^9 — mutually-independent — a hydrogen atom. The alkyl group of the carbon numbers 1-10 or the hydroxalkyl group of the carbon numbers 1-10 is expressed, A^- — a hydroxide ion or acid ion — expressing — expressing] showing the basis expressed, the substitution rate of the basis P is several/(sum total of number [of the benzene rings], and number of bases Z) =0.2-4.0 of the basis P, n expresses the integer of 0, or 1-29, and m expresses the integer of 0, or 1-10.]

[Claim 2] The metal surface treatment according to claim 1 which is a vanadium compound of trivalent [vanadium compounds / at least some / (a)] in the oxidation number of vanadium, or tetravalence.

[Claim 3] The metal surface treatment according to claim 1 or 2 which contains an organic high polymer (d) of the weight average molecular weight 1,000-1,000,000 by solution or a dispersion state.

[Claim 4] Metal surface treatment given in any 1 paragraph of claims 1-3 containing a water-soluble organic compound (e) which has at least one sort of functional groups chosen from a group which consists of a hydroxyl group, a carbonyl group, a carboxyl group, a phosphate group, a phosphonic acid group, the 1-3rd class amino group, and an amide group.

[Claim 5] Metal surface treatment given in any 1 paragraph of claims 1-3 containing at least one sort of fluorine compounds (f) chosen from fluoride and ** fluoride.

[Claim 6]A surface treatment method of a metallic material carrying out stoving so that temperature of said material may be 50-250 ** after processing the metallic material surface by metal surface treatment of a statement in any 1 paragraph of claims 1-5.

[Claim 7]A surface treatment metallic material which has the coat formed using the surface treatment method according to claim 6.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the metal surface treatment and the metal finishing method of using in order to make the coat which can give the sheet coil made from metal, the corrosion resistance excellent in the surface of mold goods, alkali resistance, and anti-fingerprint property, and does not contain chromium form, and the metallic material by which the surface treatment was carried out. An automatic car body with this invention made from a zinc system galvanized steel sheet, a steel plate, and an aluminum system metallic material with which in more detail, it is related with the finishing agent and surface treatment method which are used in order to make the coat to which corrosion resistance, alkali resistance, and anti-fingerprint property excellent in fabricating-operation articles, such as parts for autoparts, building materials, and household appliances, the cast, the sheet coil, etc. are made to give, and which does not contain chromium form, and the metallic material by which the surface treatment was carried out.

[0002]

[Description of the Prior Art] Metallic materials, such as a zinc system galvanized steel sheet and a steel plate, oxidize with the ion etc. which are contained in oxygen in the atmosphere, moisture, and moisture, and are corroded. There is a method of contacting the metallic material surface to the treating solution containing chromium, such as chromic acid chromate, conventionally as a method of preventing these corrosion, and depositing a chromate film, or making it apply and dry, and making a chromate film form in a surface of metal; however, the chromate film of these inorganic systems — if independent, although short-term rust prevention is demonstrated, under comparatively mild environment, it continues at a long period of time — or the corrosion resistance in severer environment is insufficient. Since it is weak and the formed coat is lacking in lubricity/hard when the fabricating operation of the sheet coil which performed chromate independent processing is cut down and carried out, a coat falls out, it not only spoils appearance, but it cannot perform sufficient processing but the fault of cracking a raw material and being divided into it arises. Even if a worker's fingerprint adheres at the time of work, and it carries out degreasing/washing, in order that the trace may remain, there is also fault which spoils appearance. Then, generally, in order to satisfy all the performances, such as high corrosion resistance, anti-fingerprint property, a sex with a crack-proof, lubricity, and paint adhesion, two-layer processing which forms a chromate film in the metallic material surface, and provides resin membrane further on the formed chromate film is performed. Since the chromate film is efficiently insufficient and also has hexavalent chromium harmful in the treating solution, it requires time and effort and cost for waste water treatment, and also since it contains hexavalent chromium also in the formed coat, it is in the tendency kept at arm's length from an environmental aspect and a safety aspect.

[0003] As a trial which is going to satisfy all the performances to one-layer processing, Chromate and resin membrane are examined by the resin chromate made to form at once, and them to JP,4-2672,B. To the disposal method and JP,7-6070,B which apply the resin composition which blended a specific moisture powder system or water soluble resin, and the hexavalent chromium of the specific amount with the surface of the aluminum galvanized steel sheet. The metal finishing composition containing the acrylic emulsion which polymerized on 6 value chromium ions or 6 value chromium ions and trivalent chromium ions, and the specific emulsion-polymerization conditions of the inorganic compound is indicated. However, as mentioned above, the hexavalent chromium contained in a coat is little, but it has the character which it begins to solve gradually, and has a problem in the environmental aspect and the safety aspect.

[0004]As a method of using the non chromate treatment liquid which does not have chromium, A polymer composition for metallic material surface treatment and a surface treatment method which contain the phenol resin system polymer and acidic compound of specific structure in JP,7-278410,A, Metal surface treatment and a disposal method which were mutually excellent in the anti-fingerprint property containing two or more sorts of silane coupling agents which have a reactive functional group of specific structure which can react mutually by different species, etc, at JP,8-73775,A, Metal surface treatment and a disposal method which contain the silane coupling agent of specific structure, and the phenol resin system polymer of specific structure in JP,9-241576,A, The epoxy resin which has at least one nitrogen atom in JP,10-1789,A, The metal surface treatment containing organic high polymers, such as an acrylic resin and urethane resin, and a specific multivalent anion, The rust-proofer which contains bisphenol A epoxy system resin of (1) specific structure in a disposal method and a processing metallic material, and JP,10-60233,A, (2) The disposal method and processing metallic material using the rust-proofer which contains phenol system resin and specific resin, such as the other polyester, by a specific ratio, (1), and (2) are indicated.

[0005]However, in the metal finishing which does not use chromium, While there is an advantage to which a treating solution does not contain hexavalent chromium, it has the fault that corrosion resistance is insufficient, the corrosion resistance of the crack part and the processing section is remarkably inferior compared with the chromate film especially, and anti-fingerprint property, a sex with a crack-proof, and lubricity are also insufficient. Therefore, under the present circumstances, the metal surface treatment of a non chromate system which forms the coat which can give simultaneously corrosion resistance, alkali resistance, and anti-fingerprint property excellent in the metallic material surface is not obtained.

[0006]

[Problem(s) to be Solved by the Invention]This invention was accomplished in order to solve the problem which said conventional technology has, and it is ****. the purpose is to provide the metal surface treatment, the metal finishing method, and surface treatment metallic material which are used in order to give the corrosion resistance, the alkali resistance, and anti-fingerprint property which were alike and excellent and which do not contain chromium.

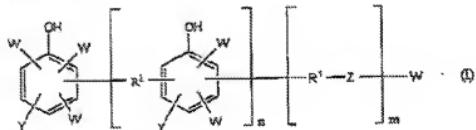
[0007]

[Means for Solving the Problem]this invention person by processing the metallic material surface using a finishing agent which uses as an essential ingredient a resin

compound which has a specific structure, a vanadium compound, and specific metallic compounds as a result of examining wholeheartedly a means to solve said SUBJECT. It finds out that a coat which has outstanding corrosion resistance, alkali resistance, and anti-fingerprint property is obtained, and came to complete this invention. Namely, a resin compound (a) in which metal surface treatment of this invention has the structure expressed with following general formula (I). Metallic compounds (c) containing at least one sort of metal chosen from a group which consists of at least one sort of vanadium compounds (b), a zirconium and titanium, molybdenum, tungsten, manganese, and cerium are contained.

[0008]

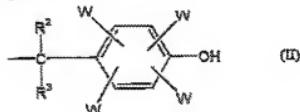
[Formula 4]



[0009]X are synonymous with X under definition of the below-mentioned W among type, each R¹ expresses -CH₂-, -CH₂-NH-CH₂-, or -CH=N-CH₂- mutually-independent, and Y is a hydrogen atom or general formula (II).

[0010]

[Formula 5]



[0011]It means (R² and R³ express the alkyl group of a hydrogen atom or the carbon numbers 1-3 mutually-independent among a formula), . Z was made by losing the hydrogen atom combined with the carbon atom which constitutes the aromatic ring from aromatic compounds which can carry out addition condensation to formaldehyde. . It may have 1-4 bases-CH₂X (X in a formula is synonymous with X under definition of the below-mentioned W). Whether the aromatic ring group in the structure bundled with n is a different divalent basis, melamine, It is the divalent basis made by losing one hydrogen atom at a time from two amino groups, guanamine or urea, W is a hydrogen atom or the basis P each mutually-independent — this — P

-CH₂X. - The inside of a CH₂NHCH₂X or -CH=NCH₂X [type and X are OH, OR⁴ (R⁴ expresses the alkyl group of the carbon numbers 1-5, or the hydroxylalkyl group of the carbon numbers 1-5), a halogen atom, general formula (III), or (IV)].

[0012]

[Formula 6]



[0013]the inside of a formula, R^6 , R^8 , R^7 , R^6 , and R^9 — mutually-independent — a hydrogen atom. The alkyl group of the carbon numbers 1-10 or the hydroxylalkyl group of the carbon numbers 1-10 is expressed, A^- — a hydroxide ion or acid ion — expressing — expressing] showing the basis expressed, the substitution rate of the basis P is several/(sum total of number [of the benzene rings], and number of bases Z) =0.2-4.0 of the basis P, n expresses the integer of 0, or 1-29, and m expresses the integer of 0, or 1-10.]

[0014]As for the vanadium compound (b) in the metal surface treatment of this invention, it is preferred that at least the part is a vanadium compound of trivalent in the oxidation number of vanadium or tetravalence from high-corrosion-resistance maintenance of the coat formed from the processing agent of this invention, and an alkali-proof point. It is preferred that the metal surface treatment of this invention contains the organic high polymer (d) of the weight average molecular weight 1,000-1,000,000 by the solution or a dispersion state as further ingredient from the point which improves corrosion resistance, anti-fingerprint property, and processability further.

[0015] Metal surface treatment of this invention as further Ingredient A hydroxyl group, a carbonyl group, Containing a water-soluble organic compound (e) which has at least one sort of functional groups chosen from a group which consists of a carboxyl group, a phosphate group, a phosphonic acid group, the 1-3rd class amino group, and an amide group, It is desirable in order to make a still more uniform coat easy to return this to tetravalence or trivalent in using a pentavalent vanadium compound, and/or to raise the stability of a vanadium compound in a treating solution of this invention, and to form. It is preferred from adhesion increase of an etching surface-of-metal reaction promotion coat of a surface of metal that metal surface treatment of this invention contains at least one sort of fluorine compounds (f) chosen from fluoride and ** fluoride as further ingredient.

[0016] This invention relates to a surface treatment method of a metallic material carrying out stoving so that temperature of said material may be 50-250 °C again, after processing the metallic material surface by said metal surface treatment. This invention relates to a surface treatment metallic material which has again the coat formed using said surface treatment method.

[0017]

[Embodiment of the Invention] As an alkyl group of the carbon numbers 1-3 which R² and R³ express, a methyl group, an ethyl group, a propyl group, and an isopropyl group are mentioned during the definition of Y of general formula (I) about the resin compound (a) made to contain in the metal surface treatment of this invention. . In general formula (I), Z was made by losing the hydrogen atom combined with the carbon atom which constitutes the aromatic ring from aromatic compounds which can carry out addition condensation to formaldehyde like previous statement. It may have 1-4 bases-CH₂X (X in a formula is synonymous with X under definition of the below-mentioned W). Although the aromatic ring group in the structure bundled with n is a different divalent basis or it is the divalent basis made by losing one hydrogen atom at a time from two amino groups of melamine, guanamine, or urea, As aromatic compounds which can carry out addition condensation to the above-mentioned formaldehyde, Although there is no limitation in particular, they are phenolsulfonic acid and alkylene glycol phenol ether (as an alkylene group), for example. Aromatic compounds, such as carbon number ON ***, the beta-naphthol, naphthalene sulfonic acid, toluene, xylenes, aniline, an acetanilide, a thiophenol, a thiophene, furfural, and furfuryl alcohol, are mentioned.

[0018] In the definition of X under definition of W of general formula (I), as an alkyl group of the carbon numbers 1-5 which R⁴ expresses, A methyl group, an ethyl group, a propyl group, an isopropyl group, a butyl group, an isobutyl group, a pentyl group, an isopentyl group, etc. as a hydroxalkyl group of the carbon numbers 1-5, A hydroxymethyl group, 2-hydroxyethyl group, 1-hydroxyethyl group, 3-hydroxypropyl group, 4-hydroxybutyl group, 5-hydroxypentyl group, etc. are mentioned. In the definition of X under definition of W of general formula (I), a chlorine atom, a bromine atom, iodine atoms, and a fluorine atom are mentioned as a halogen atom.

[0019] In the definition of X under definition of W of general formula (I), as an alkyl group of the carbon numbers 1-10 which R⁵, R⁶, R⁷, R⁸, and R⁹ ** expresses, A methyl group, an ethyl group, a propyl group, an isopropyl group, a butyl group, an isobutyl group, A pentyl group, a hexyl group, a heptyl group, an octyl group, a nonyl group, a decyl group, etc. as a hydroxalkyl group of the carbon numbers 1-10, A

hydroxymethyl group, 2-hydroxyethyl group, 1-hydroxyethyl group, 3-hydroxypropyl group, 4-hydroxybutyl group, 5-hydroxypentyl group, 6-hydroxy hexyl group, 7-hydroxy heptyl group, 8-hydroxyoctyl group, 9-hydroxynonyl group, 10-hydroxy decyl group, etc. are mentioned. In the definition of X under definition of W of general formula (I), organic acid ions, such as inorganic acid ion, such as halogen ion, sulfate ion (a chloride ion, a bromine ion, a fluorine ion, etc.), nitrate ion, and phosphoric acid ion, acetate ion, and formic acid ion, are mentioned as acid ion which A^- expresses.

[0020]A structure united at random also with block structure or a structure united by turns may be sufficient as the resin compound expressed with general formula (I) about the repeating unit bundled with n and m.

[0021]If the carbon number of the alkyl group of R^2 in Y and R^3 exceeds 3 in general formula (I), hydrophobicity will become high too much. When the abundance in the resin compound (a) of the basis P in W separates from the range of several/(sum total of number [of the benzene rings], and number of bases Z) = 0.2 of the basis P = 4.0, it becomes impossible to acquire sufficient corrosion resistance and alkali resistance. If the carbon number of the alkyl group of R^4 under definition of the basis X or a hydroxylalkyl group exceeds 5, the stability of a processing agent will fall. Similarly, if the carbon number of the alkyl group of $R^2 - R^3$ or a hydroxylalkyl group exceeds 10 by general formula (III) and (IV), the stability of a processing agent will fall. If n exceeds 29, viscosity will become high too much and the stability of the resin compound (a) in the inside of a processing agent will fall.

[0022]The resin compound (a) expressed with general formula (I) is a known compound in itself, or is a compound which a person skilled in the art can manufacture easily. Namely, give the basis Z further to phenol, the bisphenol system compound, or this which does not have whether it has the substituent P. Addition condensation of what added ammonia to what added the compound which can carry out addition condensation to formaldehyde, formaldehyde, or this further can be carried out, and it can obtain by [which change into the thing aiming at W basis if needed] carrying out.

[0023]Since the solubility in the inside of this metal surface treatment of a resin compound (a) or dispersibility is improved, an ^{old} component, for example, phosphoric acid, chloride, ^{old} sulfuric acid, nitric acid, formic acid, acetic acid, etc. can add an alkali component, for example, sodium hydroxide, a potassium hydrate, ammonia, 1 - tertiary amine, etc.

[0024]The vanadium compound (b) made to contain in the metal surface treatment of this invention, The oxidation number of vanadium Pentavalence and tetravalent or trivalent vanadium compound, for example, vanadium pentoxide V_2O_5 , Meta-vanadium acid HVO_3 , ammonium metavanadate, sodium metavanadate, Vanadium compounds of

oxidation number pentavalence, such as vanadium trichloride oxide VOCl_3 , Vanadium trioxide V_2O_3 , vanadium dioxide VO_2 , Oxyvanadium sulfate VOSO_4 , vanadium oxyacetyl acetate $\text{VO}(\text{OC}(\text{=CH}_2)\text{CH}_2\text{COCH}_3)_2$, Vanadium acetyl acetate $\text{V}(\text{OC}(\text{=CH}_2)\text{CH}_2\text{COCH}_3)_3$, It is at least one sort chosen from the vanadium compound of oxidation number trivalent or tetravalence, such as vanadium trichloride VCl_3 , phosphorus BANADO molybdic acid $\text{H}_{15-x}[\text{PV}_{12-x}\text{Mo}_x\text{O}_{46}]_{n/2}\text{H}_2\text{O}$ ($6 \leq x \leq 12$, $n \leq 30$), etc.

[0025]It is preferred that this processing agent contains the vanadium compound of oxidation number trivalent or tetravalence as a vanadium compound (b) from high-corrosion-resistance maintenance of the coat formed, and an alkali-proof point. Namely, the rate of the vanadium compound of oxidation number trivalent or tetravalence of occupying to a vanadium compound (b), $(\text{V}^{3+}+\text{V}^{4+})$ as V (V^{3+} , V^{4+} , and V express the oxidation number trivalent vanadium mass in a vanadium compound (b), the vanadium mass of oxidation number tetravalence, and total vanadium mass among a formula, respectively), desirable — 0.1—1.0 — further — desirable — 0.2—1.0 — it is 0.4—1.0 most preferably.

[0026]As a method of making a trivalent or tetravalent vanadium compound containing in this processing agent, a trivalent or tetravalent vanadium compound which was described above is used, and also what returned the pentavalent vanadium compound to trivalent or tetravalence using the reducing agent beforehand can be used. the reducing agent to be used — an inorganic system and an organic system — although any may be sufficient, an organic system is preferred and especially the thing for which a water-soluble organic compound (e) is used is preferred.

[0027]The water-soluble organic compound (e) made to contain in the metal surface treatment of this invention if needed, It is a water-soluble organic compound which has at least one sort of functional groups chosen from the group which consists of a hydroxyl group, a carbonyl group, a carboxyl group, a phosphate group ($-\text{OPO}_3\text{H}_2$), a phosphonic acid group ($-\text{PO}_3\text{H}_2$), the 1—3rd class amino group, and an amide group. As this water-soluble organic compound (e), methanol, ethanol, Alcohols, such as isopropanol and ethylene glycol; Formaldehyde, Aldehyde compounds, such as acetaldehyde and furfural; An acetylacetone, Carbonyl compounds, such as ethyl acetoacetate, dipivaloyl methane, and 3-methylpentanediol; Formic acid, Acetic acid, propionic acid, tartaric acid, ascorbic acid, gluconic acid, citrate, Organic acid, such as malic acid; Triethylamine, triethanolamine, ethylenediamine, Amine compounds, such as pyridine, imidazole, pyrrole, morpholine, and a piperazine; A formamide, Acid amide compounds, such as an acetamide, propionamide, and N-methylpropionamide; A glycine, Amino acid, such as an alanine, pyrrolidine, and glutamic acid; Glucose, mannose,

Monosaccharides, such as galactose; Natural polysaccharide; friend NOTORI, such as maltose, sucrose, starch, and cellulose (methyleno phosphonic acid), Organic phosphorus acid, such as 1-hydroxyethylidene-1,1-diphosphonic acid, ethylenediamine tetra (methyleno phosphonic acid), and phytic acid; Gallic acid, tannic acid, humic acid, ligninsulfonic acid, Naturally-occurring polymers, such as polyphenol; aminocarboxylic acid, such as synthetic macromolecule;EDTA, such as polyvinyl alcohol, a polyethylene glycol, polyacrylic acid, polyacrylamide, polyethyleneimine, and water-soluble nylon, etc. are mentioned.

[0028]These water-soluble organic compounds (e) can raise the stability of the vanadium compound in a treating solution remarkably, and they not only can have the operation which returns a vanadium compound, but can maintain the corrosion-resistant grant effect which was excellent in the processing agent of this invention for a long time. Since there is an effect also in uniform coat formation, a corrosion-resistant level can also improve. If the water-soluble organic compound (e) has said functional group, it will demonstrate an effect, but what has at least one sort of two or more functional group numbers per molecule chosen from said functional group is more preferred. Although it can mix with a processing agent simply and can also use about the application method to this processing agent of a water-soluble organic compound (e), It is more preferred to apply the mixture which was beforehand mixed with the vanadium compound, heated (it is 5 to 120 minutes at 40-100 **), and fully advanced the reduction reaction and the stabilization reaction.

[0029]The zirconium, titanium which are made to contain in the metal surface treatment of this invention. The metallic compounds (c) containing at least one sort of metal chosen from the group which consists of molybdenum, tungsten, manganese, and selenium are salts with the oxide of said metal, hydroxide, a complex compound, inorganic acid, or organic acid, etc., and it is preferred that said resin compound (a) and compatibility are good. As these metallic compounds (c), for example Zirconium nitrate $ZrO(NO_3)_2$, Zirconium sulfate and carbonic acid zirconyl ammonium $(NH_4)_2[Zr(CO_3)_2(OH)_2]$, Titanyl sulfate $TiSO_4$, diisopropoxy titanium screw acetylacetone $(C_6H_5O_2)_2Ti[OCH(CH_3)_2]$, The reactant of lactic acid and a titanium alkoxide, titanium lactate $(OH)_2Ti(O_2H_2O_2)_2$, Molybdic acid H_2MoO_4 , ammonium molybdate, sodium molybdate, a molybdophosphoric acid compound (for example, molybdophosphoric acid ammonium $(NH_4)_2[PO_4Mo_12O_38]$ and $3H_2O$) Sodium-molybdophosphate $Na_2[PO_4\text{and}12MoO_3] \cdot nH_2O$ etc., Meta-tungstic acid $H_5[H_2W_12O_42]$, ammonium metatungstate $(NH_4)_6[H_2W_12O_42]$, meta-sodium tungstate, and Para tungstic acid $H_{10}[W_12O_42H_10]$, Ammonium paratungstate, Para sodium tungstate.

Fault man can acid HMnO_4 , potassium permanganate, sodium permanganate, Phosphoric acid 2 hydrogen manganese $\text{Mn}(\text{H}_2\text{PO}_4)_2$, manganese nitrate $\text{Mn}(\text{NO}_3)_2$, Manganese(II) sulfate, (III) or (IV), manganese fluoride (II), or (III), Manganese carbonate and manganese acetate (II) or (III), cerium acetate $\text{Ce}(\text{CH}_3\text{CO}_2)_3$, cerium nitrate (III) or (IV), cerium chloride, etc., are mentioned. About a molybdenum (VI) compound, a tungsten (VI) compound, and a manganese (VI) compound, it is usable also in what was returned using reducing agents, such as alcohols and organic acid.

[0030]As for the organic high polymer (d) made to contain by the solution or a dispersion state in the metal surface treatment of this invention if needed, it is preferred that it is a thing of the weight average molecular weight 1,000-1000, and 000. More desirable molecular weights are 2,000-500,000. If less than 1,000 are [said molecular weight] insufficient as for film-forming and it exceeds 1000 and 000, it will become the cause of reducing the stability of a processing agent. It is what makes a distributed form like an emulsion and dispersion under existence of the thing which can mix this organic high polymer (d) in a processing agent, and may be dissolved in water, itself, or an emulsifier, if it exists stably in a processing agent, and uniformly and the gestalt in which water dilution is possible can be taken, it can be especially used without restriction. Above, ~~about~~ not limited especially as an emulsifier, nonionic surface-active agents, such as cationic surface-active agents, such as anionic surface-active agents, such as alkyl sulfate, and alkyl quaternary ammonium salt, and alkylphenyl ether, a water soluble polymer, etc. can be used, for example.

[0031]The synthetic macromolecule which may be made to contain by the solution or a dispersion state as an example of this organic high polymer (d), for example, alkyl acrylate (meta-) (carbon numbers 1-8) ester (methyl acrylate) Methyl methacrylate, ethyl acrylate, ethyl methacrylate, Propylacrylate, butyl acrylate, 2-ethylhexyl methacrylate, acrylic acid (meta-) hydroxyalkyl (carbon numbers 1-4) ester (2-hydroxyethyl (meta-) acrylate), such as octyl acrylate Independent or the copolymer of acrylic monomers, such as acrylic acid (meta), such as 3-hydroxypropyl (meta) acrylate, This acrylic monomer (30 % of the weight or more) and styrene, acrylonitrile, acrylic resin [such as a copolymer with addition condensation nature unsaturated monomers, such as vinyl acetate,]; — an olefin (carbon numbers 1-8) (ethylene) Polyolefin system resin, such as a copolymer of independent or copolymers, such as propylene, a butene, a hexene, and octene, this olefin (50 % of the weight or more), acrylic acid (meta), etc., etc.;

[0032]alkylene (carbon numbers 1-6) glycol (ethylene glycol and propylene glycol) A butylene glycol, neopentyl glycol, hexamethylene glycol, etc., polyether polyol

(polyethylene glycols, such as a diethylene glycol and triethylene glycol,) polyester polyol (above alkylene glycol or polyether polyol), such as polyethylene/propylene glycol Bisphenol A, hydrogenation bisphenol A, trimethylolpropane, Polyols, such as glycerin, succinic acid, glutaric acid, adipic acid, sebatic acid, The polyester polyol which has a hydroxyl group at the end obtained by a polycondensation with polybasic acid, such as phthalic acid, isophthalic acid, terephthalic acid, and trimellitic acid, polyols, such as polycarbonate polyol, aromatic series, alicyclic, or aliphatic series polyisocyanate (tolylene diisocyanate.) Urethane resin which is a polycondensation thing with diphenylmethane diisocyanate, xylylene diisocyanate, dicyclohexylmethane diisocyanate, cyclohexylene diisocyanate, hexamethylene di-isocyanate, lysine diisocyanate, etc.;

[0033]The bisphenol type epoxy resin produced by making bisphenols especially bisphenol A, and epichlorohydrin react is made into the start, The novolak type epoxy resin which glycidyl-ether-ized the phenolic hydroxyl group of phenol novolak resin, Epoxy resins, such as a peroxy-acid epoxy type epoxy resin which epoxidated glycidyl ester of aromatic carboxylic acid, and the double bond of the ethylenic unsaturated compound with the peroxy acid; Ethylene glycol, Polyester resin; etc. which are the condensates of polyol ingredients, such as neopentyl glycol, and polybasic acid, such as terephthalic acid and trimellitic anhydride, are mentioned.

[0034]The soap-free who does not use the surface-active agent as a solubilizing agent and an emulsification dispersion agent in these organic high polymers (d), Or more, what was stopped as much as possible is [the amount used] preferred, and it about acrylic resin. Anionic hydrophilic groups, such as a sulfonic group, a phosphate group, a phosphonic acid group, and a carboxyl group. Cationic hydrophilic groups, such as the 1st - the 3rd class amino group, and the 4th ammonium. Carry out copolymerization of the monomer which has at least one sort of hydrophilic groups chosen from nonionic hydrophilic groups, such as a hydroxyl group, a polyoxyethylene chain, and an amide group, and Aqueous-izing. Or it is more preferred to make the thing which carried out self-emulsification, or the reactive surface active agent which has an unsaturated bond add at the time of a polymerization, and to carry out self-emulsification. In urethane resin using the monomer which has said hydrophilic group about polyolefin system resin as a copolymer component, In the epoxy resin using what has a hydrophilic group which does not react to one of the polyol ingredients among said hydrophilic groups at the time of a polymerization, Resin of water solubility and self-emulsifiability can be obtained using the polybasic acid which has said hydrophilic group for some polybasic acid which denaturalizes a part or all of

glycidyl ether, and introduces said hydrophilic group and which is used in polyester resin.

[0035] At least one sort of fluorine compounds (f) chosen from the group which consists of the hydrofluoric acid, metal fluoride, and ** fluoride which are applied to this invention finishing agent, Hydrofluoric acid, fluoroboric acid, hydrofluosilic acid, zirconium hydrofluoric acid, titanium hydrofluoric acid, stannous fluoride, the first iron of fluoridation, ferric fluoride, etc. can be used with the compound which gives the fluorine ion separated in solution by the etching agent of raw material metal, and fluoride ion.

[0036] The quantity of each constituent in the processing agent of this invention is described below about the case where a resin compound (a), (solid content), vanadium in a vanadium compound (b), the metal in metallic compounds (c), and the sum total of an organic high polymer (d), (solid content), and a water-soluble organic compound (e) are made into 100 mass %. As solid content, 3 - 99 mass % of a resin compound (a) is preferred, and its 5 - 95 mass % is more preferred, 0.05 - 30 mass % of a vanadium compound (b) is preferred as vanadium, and its 0.1 - 20 mass % is more preferred. 0.05 - 30 mass % of metallic compounds (c) is preferred as metal, and its 0.1 - 20 mass % is more preferred. As solid content, 5 - 95 mass % of an organic high polymer (d) is preferred, and its 10 - 80 mass % is more preferred. About a resin compound (a), a vanadium compound (b), metallic compounds (c), and an organic high polymer (d), in order to maintain high corrosion resistance, to choose the above-mentioned desirable range, respectively is desired. Because of the stability maintenance in the inside of the treating solution of a vanadium compound (b), a water-soluble organic compound (e) has preferred 5 - 400 mass % to vanadium of a vanadium compound (b), and its 10 - 300 mass % is more preferred. 0.05-30 g/L of a fluorine compound (f) is preferred in a processing agent, and its 0.1-20 g/L is more preferred. As for a reaction with a raw material, less than 0.05 g/L is insufficient, when it exceeds 30 g/L etching is superfluous and there is a tendency which checks adhesion. [0037] water-dispersion silica in order to adjust coat physical properties, such as corrosion-resistant improvement in a coat, and tensile strength, in the processing agent of this invention --- sol. and/or, alumina sol and zirconia --- the quantity which it is effective to add metal sols, such as sol, and it adds in this case, About the same standard as the above, i.e., when a resin compound (a), (solid content), vanadium in a vanadium compound (b), the metal in metallic compounds (c), and the sum total of an organic high polymer (d), (solid content), and a water-soluble organic compound (e) are made into 100 mass %, 5 - 40 mass % is preferred as solid content, and 10 - 30 mass % is more preferred. In the

processing agent of this invention, in order to raise the lubricity of a coat, and processability A polyolefin system wax. It is effective to make at least one sort chosen from drainage system waxes, such as an ester system wax and a hydrocarbon system wax, contain, about the same standard as the above, the quantity added in this case has preferred 0.5 - 30 mass % as solid content, and its 1 - 20 mass % is more preferred. The organic cross linking agent and the inorganic cross linking agent which can construct a bridge in an organic polymer compound (d) into the finishing agent of this invention can be added. As an organic cross linking agent, an epoxy system, a melamine system, an aldehyde system, and an isocyanate system are used. As an inorganic cross linking agent, the compound of metal, such as iron other than the metallic compounds specified by this invention, cobalt, nickel, niobium, tantalum, and zinc, is mentioned.

[0038] Although the solvent used by the finishing agent of this invention makes water a subject, it does not bar concomitant use of the water soluble organic solvent of alcohol, ketone, and a cellosolve system if needed [, such as a drying improvement of a coat,]. In addition, it can add in the range which does not spoil the meaning or coat performance of this inventions, such as a surface-active agent, a defoaming agent, a leveling agent, an antimicrobial antibacterial, and colorant.

[0039] Next the surface treatment method of this invention is described. After applying processing agent liquid on the surface of a metal material about a disposal method, it will not matter, if stoving can be carried out at 50-250 **, and does not specify about a coating method and a drying method. Usually, the method of extracting with a roll after a flow coating beam by the roll coat method for making a material surface carry out roll transfer, and plastering it with a processing agent or a shower ringer, or carrying out the liquid end with an air knife, the method of immersing a raw material into a treating solution, and the method of carrying out the spray of the processing agent to a raw material are used. Although the temperature in particular of a treating solution is not limited, since the water of the solvent of this processing agent is a subject, 0-60 ** of treatment temperature is preferred, and its 5-40 ** is more preferred.

[0040] Although specification is not carried out about down stream processing, either, in order to usually remove the oil and dirt adhering to a raw material before performing this processing, an alkaline-degreasing agent or an acid degreaser washes, or hot water rinsing, solvent cleaning, etc. are performed. Then, surface control by acid, alkali, etc. is performed if needed. In washing of a material surface, it is preferred to rinse after washing so that a detergent may not remain if possible to a material surface.

After washing a raw material surface of metal, the processing agent of this invention applies directly, but applying is also possible after performing chemical conversion of a phosphate system.

[0041]When it is not necessary to promote hardening of an organic high polymer (d) and performs only removal of attached groundwater, a drying process. Although heat may not necessarily be needed but physical removal of air-drying or a blowing air may be sufficient, in order to heighten the covering effect by the promotion of hardening of an organic high polymer (d), or softening, it is necessary to carry out stoving. As for the temperature in that case, 50-250 ** is preferred, and it is more preferred. [of 60-220 **]

[0042]The coating weight of the coat formed has preferred 30 - 5,000 mg/m² with total coat mass, and its 50 - 3,000 mg/m² is more preferred. If corrosion resistance sufficient by less than 30 mg/m² and adhesion with finishing are not acquired but 5,000 mg/m² is exceeded, a crack etc. will arise in a coat and the adhesion of the coat itself will fall.

[0043]

[Function]It is thought that the finishing agent of this invention reacts to a raw material surface of metal, forms the good coat of adhesion in the process which is applied to raw material metal and dried, and a resinous principle carries out film formation and it gives the outstanding corrosion resistance and paint adhesion to a raw material. In the time of processing agent application, or a stoving process, a resin compound (a), a vanadium compound (b), and metallic compounds (c) form and carry out film formation of the precise three-dimensional structure, and it reacts to a surface of metal and they adhere. Although each substituent-CH₂X specified with the resin compound (a) acts as KACHIONOIDO (-CH₂) and crosslinking reaction is carried out to the part (aromatic ring) where the electron density in a resin skeleton is high in electrophilic substitution, These KACHIONOIDO group reacts also to the part where the electron density of a surface of metal is high, and resin deposits and adheres to the surface. The specified vanadium compound (b) and the specified metallic compounds (c) all have a vacant orbital with the transition metal compound, are considered to be one sort of KACHIONOIDO, and have the character which adheres to a surface of metal similarly.

[0044]Thus, having the corrosion resistance excellent in the formed coat can consider the following thing besides being based on the surface-of-metal barrier property of the formed coat. That is, the resin compound (a) specified by this invention is a compound which has resonance stabilization structure, and a vanadium compound (b)

and the specified metallic compounds (c) are transition metal compounds, as mentioned above. The coat formed with a resin compound (a), a vanadium compound (b), and specific metallic compounds (c), Since it is a sufficiently near distance to such an extent that it laps with the coat orbit of raw material metal by reacting to a surface of metal and adhering, it has the operation which delocalizes the electron produced by corrosion using phi orbit, and surface potential is kept uniform by this and to give the outstanding corrosion resistance (not only a flat-surface part but an amputation stump side, a crack part) is considered. Although chromium of existing soluble 6 values begins to melt and the self-remedial action which re-deposits in a surface-of-metal exposed part is generally said, the corrosion prevention mechanism of the conventional chromate film, This invention persons think that the corrosion prevention mechanism of a chromate film is the same corrosion prevention mechanism as the high KACHIONOIDO nature (high adherence reactivity to a surface of metal) of chromium, and the processing agent of this invention resulting from the outstanding delocalization operation (corrosion electron).

This invention is accomplished based on these ideas.

[0045]An organic high polymer (d) is formed on said coat formed in the metal interface (that is, it has two-layer structure), there is a corrosion-resistant improved effect by improving barrier property, and also there is an effect which improves anti-fingerprint property, processability, etc. By etching a metal material, a fluorine compound (f) promotes a reaction with the surface of metal of a resin compound (a), a vanadium compound (b), and specific metallic compounds (c), and is effective in making a coat with higher adhesion form. A water-soluble organic compound (e) returns vanadium of oxidation number pentavalence to oxidation number tetravalence or trivalent, and has the operation which carries out chelate stabilization of these reduced forms, it continues at a long period of time, a processing agent is kept stable, and it is thought that there is an operation which improves the water resisting property of the coat after stoving and alkali resistance.

[0046]

[Example]Next, although an example and a comparative example explain this invention, this example is only a mere example and does not limit this invention. The valuation method about the processing board sample produced in the example and the comparative example is as follows.

1. Raw material A : electro-galvanizing steel plate (board thickness: 0.8 mm)

B: Hot-dip zinc-coated steel sheet (board thickness: 0.8 mm)

C:55% aluminum galvanized steel sheet (board thickness: 0.5 mm)

2. The resin compound (a) which was used for the treating solution (1) treating-solution ingredient example and which is expressed with general formula (I) is as being shown in Table 1.

[0047]

[Table 1]

表1

	R ₁	W	Y	Z	n	m
a 1	①	① ②(2.0)	①	---	1	0
a 2	①	① ②(2.0) ③(0.5)	①	---	2	0
a 3	① ②	① ②(0.2) ⑦(1.0)	①	---	10	0
a 4	①	① ②(0.2) ③(0.2) ⑥(0.4)	① ②(0.5)	---	5	0
a 5	①	① ⑤(0.5)	③(1.0)	---	15	0
a 6	① ②	① ③(0.4) ⑦(1.0)	①	---	10	0
a 7	①	① ⑤(0.6)	① ②(0.2)	---	20	0
a 8	① ③	① ②(0.1) ③(2.0)	①	①	5	1
a 9	①	① ⑥(0.8)	① ③(0.8)	②	8	5

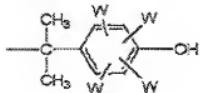
括弧内は、Wについては基Pの数/（ベンゼン環の数、及び基Zの数の合計）を、Yについては、ベンゼン環1個に対するYの當量数を示す。

[0048]In Table 1, **** expresses a following meaning about each basis.R₁-①-CH₂-②-CH₂-NH-CH₂-W-④H-CH₂OH-CH₂OCH₃-CH₂Br-⑤-CH₂N(CH₃)(CH₂CH₂OH)

① ② ③ ④ ⑤

① $\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$, ② CH_2NH_2 , ③ $\text{CH}_2\text{N}^+(\text{CH}_3)_3$, and $\text{OH}^-\text{Y}^+\text{H}^+$ [0049]

[Formula 7]



[0050] Aromatic compounds used as the basis of Z basis: ** aniline ** furfuryl alcohol

[0051] The used vanadium compound (b) is described below.

b1: Describe below the metallic compounds (c) which carried out vanadium pentoxide

b2: ammonium metavanadate b3: vanadium trioxide b4: vanadium oxy acetylacetone use.

c1: zirconium carbonate ammonium c2: — zircon — fluoric acid c3: Para ammonium molybdate c4: ammonium metatungstate c5: titanium laurate c6: — manganese carbonate [0052] The used organic high polymer (d) is described below.

d1: Acrylic emulsion (Showa High Polymer Co., Ltd. make and polysoal AP6530)

d2: Acrylic emulsion (the Showa High Polymer Co., Ltd. make, polysoal AM-2386)

d3: Cation modified epoxy resin (the Asahi Denka Kogyo K.K. make, ADEKA resin EM-440)

d4: Drainage system polyurethane (the Dai-ichi Kogyo Seiyaku Co., Ltd. make, super flex time 150)

d5: Drainage system polyurethanes (the Asahi Denka Kogyo K.K. make, ADEKABON titer HUX-670)

[0053] The used reducing agent (e) is described below.

e1: L-ascorbic-acid e2:D-glucose e3: Glyoxal e4: friend NOTORI (methylene phosphonic acid)

The used fluorine compound (f) is described below.

f1: $\text{HF}_2\text{H}_2\text{ZrF}_6$ f2: H_2TlF — the other ingredients (g) used in order to adjust pH of a f4: H_2SiF_6 processing agent are described below.

g1: ammonia g2: — phosphoric acid [0054](2) After stirring the solution or the water dispersion which mixed the preparation vanadium compounds (b) and organic compound (e) of the treating solution at 20-90 ** for 20 to 120 minutes, Fluorine compound (f) solution and metallic-compounds (c) solution were added under stirring after cooling to a room temperature, the resin compound (d) was added, and, finally the water diluent of the organic high polymer (d) was added. [0055]3. the alkaline-degreasing agent PAL by disposal method (1) degreasing Nihon Parkerizing Co., Ltd. — clean —

after degreasing a raw material by 364S (20 g/L initial make-up of electrolytic bath, 60 **, 10-second spray, and spray pressure 0.5kg/cm²), spray rinsing was performed for 10 seconds.

(2) Spreading and desiccation I: bar coat spreading of the treating solution adjusted to concentration 16 mass % was carried out so that dry membrane thickness might be set to 1 micro, and it dried at 80 ** (PMT).

II: Bar coat spreading of the treating solution adjusted to concentration 16 mass % was carried out so that dry membrane thickness might be set to 1 micro, and it dried at 150 ** (PMT).

[0056]4. The corrosion resistance test was done about unprocessed (flat-surface part) about the processing board sample produced in the valuation method (1) corrosion-resistance example and the comparative example, the thing (crosscut part) which carried out the cross cut till base attainment by NT cutter, and the thing (processing section) which carried out Erichsen 7-mm extruding. The valuation method is as follows.

(Flat-surface part) Based on neutral salt spray test method JIS-Z-2371, it evaluated in quest of the white rust generating area 72 hours after a salt fog.

Valuation basis: Based on ** not less than 30% - less than 60% x white rust generating area O not less than (crosscut part) 60% neutral salt spray test method JIS-Z-2371, the white rust generation state 72 hours after a salt fog was evaluated less than 10% with the naked eye not less than 10% - O less than 30%.

valuation-basis: — white rust generation state O — almost — rust nothing and O — based on neutral salt spray test method JIS-Z-2371 with remarkable (processing section) x rust generating to which those with rust and ** rust generating are accepted slightly, the white rust generation state 72 hours after a salt fog was evaluated with the naked eye.

valuation-basis: — white rust generation state O — almost — rust nothing and O — x rust generating those with rust and ** rust generating are slightly accepted to be is remarkable [0057](2) an alkali-proof processing board sample — the alkaline-degreasing agent PAL by Nihon Parkerizing Co., Ltd. — clean — after carrying out the spray of the degreaser solution which carried out the initial make-up of electrolytic bath of 364S to 20 g/L, and was adjusted to 65 ** for 2 minutes and rinsing it, it dried at 80 **. The conditions and appraisal method which were indicated above (1) about this board estimated corrosion resistance.

(3) The finger was forced on the anti-fingerprint property processing sheet surface, and the trace state of the fingerprint was observed with the naked eye, and was

evaluated. valuation-basis: — O without O trace — x with ** trace which has a trace very slightly — the processing agent with which (4) processing agent stability example in which a trace remains clearly, and the comparative example were presented was kept to the well-closed container for three weeks at 30 **, and the state of subsequent liquid was observed.

valuation-basis: — O — x gelling in which the re dispersion possibility of and ** separated substances cannot be and carry out re dispersion easily although there are completely change nothing. O thickening, or slight separated substances [0058]The contents of a treating solution and the disposal method of Examples 1-16 and the comparative examples 1-5 were shown in Table 2, and the examination evaluation result was shown in Table 3. Examples 1-16 which consist of a coat formed using the finishing agent of this invention have treating solution stability and good anti-fingerprint property so that clearly from Table 3. Since harmful chromium is not included, safety is high, and it turns out that it has the corrosion resistance which excelled chromate treatment in both the flat-surface part the crosscut part and the processing section. On the other hand, the comparative example 1 which does not contain the resin compound (a) which is an essential ingredient of the processing agent of this invention, the comparative example 2 which did not contain a vanadium compound (b), and the comparative example 3 which did not contain metallic compounds (c) are inferior in corrosion resistance. The comparative example 4 which used the resin compound without the structure specified by this invention instead of the resin compound (a) was also inferior in corrosion resistance. Especially the comparative example 5 that carried out chromate (zinc ROM 3360H) processing was inferior in anti-fingerprint property and the corrosion resistance of the processing section after alkaline degreasing.

[0059]

[Table 2]

表2

実施例 及び 比較例	素材	処理液成分(重量%)=							処理 方法
		(a)	(b)	(c)	(d)	(e)	(f)aa	(g)aa	
実施例 1	A	a1(50)	b1(3)	c1(8)	d1(40)	e1(1)	f1(1)	—	I
実施例 2	B	a1(20)	b2(4)	c3(4)	d4(70)	e2(2)	f2(2)	—	II
実施例 3	A	a2(45)	b2(3)	c4(3)	d1(42)	e4(3)	f4(2)	g1(5)	I
実施例 4	B	a2(10)	b3(2)	c1(3)	d4(75)	e4(5)	f1(3)	—	II
実施例 5	A	a1(63)	b1(5)	c1(10)	—	e1(2)	f1(1)	—	I
実施例 6	A	a3(40)	b2(4)	c2(4)	d2(52)	—	f3(2)	—	II
実施例 7	A	a3(38)	b2(4)	c2(4)	d2(50)	e1(4)	f3(2)	—	I
実施例 8	C	a4(20)	b1(2)	c3(5)	d5(70)	—	f1(1)	—	II
実施例 9	A	a5(70)	b2(5)	c4(5)	d3(20)	e3(1)	f2(2)	g2(25)	I
実施例 10	A	a5(70)	b2(5)	c4(5)	d3(20)	e3(1)	—	g2(35)	I
実施例 11	B	a8(20)	b2(10)	c5(10)	d5(55)	e4(5)	f6(1)	—	II
実施例 12	C	a7(50)	b3(2)	c5(5)	d3(20)	—	f4(1)	g2(5)	I
実施例 13	C	a8(30)	b1(8)	c2(6)	d2(54)	e2(8)	f2(2)	g2(5)	II
実施例 14	C	a9(10)	b2(10)	c5(4)	d5(70)	e4(6)	f4(5)	—	II
実施例 15	A	a5(20)	b4(0.5)	c2(1)	d5(78.5)	—	—	g2(10)	I
実施例 16	B	a5(10)	b6(1)	c2(2)	d5(85)	e1(1)	—	g2(5)	I
比較例 1	A	実施例 1において(a)成分を用いなかった							I
比較例 2	B	実施例 2において(b)成分を用いなかった							II
比較例 3	A	実施例 3において(c)成分を用いなかった							I
比較例 4	B	実施例 2の(a)の代わりにf ₂ を用いた							II
比較例 5	A	タブレット(シアン化鉄3320H;Cr20mg/x2)							aa

*成分(a)+(b)+(c)の合計量+成分(d)+(e)の合計を100%としたときの値

**処理液 1 L 中の重量 (g/L)

***日本バーラライジング(株) 製、密度クロメートジンクロム 3360 H を Cr 付着量で
20mg/mL になるようにロールコートし、80°C (PMT) で加熱乾燥した。

表2において、成分(b)と成分(e)を併用している実施例は、何れも下記(b)と(e)を基準し、
(b)の金属分として5%となるように純水で希釈し、80°C～100°Cで約2時間加熱保持した後、
冷却したものを用いた。

Example
example

[0060]

[Table 3]

表 3

No.	評価 方法 部位	耐食性						耐 燃 性 性	処理 剤 安定性	クロム 有 害性			
		平面部		外縁部外部		加工部							
		無	有	無	有	無	有						
実施例 1	◎	◎	◎	◎	◎	◎	◎	◎	◎	○			
実施例 2	◎	◎	◎	◎	◎	◎	◎	◎	◎	○			
実施例 3	◎	◎	◎	◎	◎	◎	◎	◎	◎	○			
実施例 4	◎	◎	◎	◎	◎	◎	◎	◎	◎	○			
実施例 5	○	○	○	○	○	○	○	○	◎	○			
実施例 6	○	○	○	○	○	○	○	○	○-△	○			
実施例 7	◎	◎	○	◎	◎	◎	◎	◎	◎	○			
実施例 8	◎	◎	○	○	○	○	○	○	○-△	○			
実施例 9	◎	◎	◎	◎	◎	◎	◎	◎	◎	○			
実施例 10	○	○	○	○	○	○	○	○	◎	○			
実施例 11	◎	◎	◎	◎	◎	◎	◎	◎	◎	○			
実施例 12	○	○	○	○	○	○	○	○	○-△	○			
実施例 13	◎	◎	○	○	○	○	○	○	◎	○			
実施例 14	◎	◎	○	○	○	○	○	○	◎	○			
実施例 15	◎	◎	○	○	○	○	○	○	○	○			
実施例 16	◎	◎	○	○	○	○	○	○	◎	○			
比較例 1	△	×	×	×	×	×	×	◎	◎	○			
比較例 2	△	△	△	×	△	×	○	○	○	○			
比較例 3	○	×	○	×	○	×	○	○	○	○			
比較例 4	△	×	×	×	×	×	○	○	○	○			
比較例 5	◎	△	◎	△	△	×	×	◎	○	×			

[0061]

[Effect of the Invention] The processing agent of this invention is a non chromate type which does not contain a harmful chromium compound, and the coat formed from this finishing agent has the conventional chromate film and the corrosion resistance more than equivalent also not only in a flat-surface part but in a crack part and a processing section.

And alkali resistance and anti-fingerprint property are also excellent, and the industrial utility value of the finishing agent, surface treatment method, and surface treatment metallic material of this invention is very high.